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SEPARATION OF MOISTURE AND SULPHUR COMPOUNDS
FROM NATURAL GAS STREAMS

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95/136

This invention relates to the sweetening and drying
of natural gas, and more specifically relates to an improved
process for sweetening and drying a natural gas stream by
contact with an adsorbent material.

5   Sweetening and drying natural gas streams is ex-
tremely important to industry for several reasons. The
presence of sulfur-containing compounds in such streams may
result in the deposition of sulfur salts which can cause
plugging and corrosion of transmission pipes, valves, regula-

10   tors and the like. Also, the sulfur compounds may produce
undesirable side reactions with other materials contacting the
natural gas stream.

       Similarly, if water is not removed from the natural
gas stream, hydrocarbon-water hydrates are formed which

15   deposit as solids. Such hydrates can cause plugging of
pipelines, freezing of valves and regulators, and excessive
pressure drops in the pipelines. Furthermore, dehydration of
natural gas eliminates the need for costly and elaborate in-
jections of hydrate-suppressing alcohol or glycerol into

20   transmission conduits. For these reasons, gas transmission
companies specify that the hydrogen sulfide content of the
gas cannot exceed 4 ppm. by volume. Also, the maximum allow-
able water content varies between 84 and 190 ppm. by volume
(4 and 9 lbs. H_2O/MMSCF.) depending on the locale.

25   The tremendous increase in demand for natural gas
in recent years has made the gas producers far more de-
pendent on "sour" gas fields than ever before. As used herein,

<div align="center">2.   ✻</div>

a "sour" gas is defined as a gas containing H_2S and/or mercaptans. "Sweetening" is defined as the removal of H_2S and/or mercaptans from a gas or a liquid stream. Formerly, when a gas well came in "sour," it was capped off because

5 the supply and demand situation did not merit its purification. Recently, these capped wells have been put into production and new completions are being utilized regardless of H_2S content.

There are a number of sweetening and drying

10 processes currently being used, but they all have important and critical limitations. One widely used system involves scrubbing by monoethanolamine (MEA). The natural gas is passed through the MEA solution which absorbs the hydrogen sulfide. The solution from the absorption equipment is

15 passed to a stripping column where heat is applied to boil the solution and release the hydrogen sulfide. The lean stripped solution is then passed to heat exchangers, and returned to the absorption equipment to again absorb hydrogen sulfide gas. The principal disadvantages of the MEA system

20 are its high operating cost because of the corrosive nature of the absorbing liquid, and its inability to remove mercaptans and water from gas streams.

Another prior art system is the iron sponge method of purifying natural gas, utilizing iron oxide impregnated

25 wood chips in a packed bed. The gaseous mixture containing H_2S and/or mercaptans contacts a packed bed of iron oxide sponge, preferably chemically absorbing the sulfur impurities

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on the exposed iron oxide surface. After the bed has been saturated it is reactivated by passing heated air through the bed. One disadvantage of this method of sweetening natural gas is that a dehydration system must follow the iron sponge system to dry the gas for pipeline use. Also, the reactivation step is hazardous because of the exothermic nature of the reactivation reaction. Furthermore, fusion of iron sponge particles with sulfur frequently causes a high pressure drop through the bed. Finally, the operational cost is high because the absorbent must be replaced frequently.

Hydrogen sulfide has also been removed from natural gas by countercurrent extraction with a hot potassium carbonate solution. In this unit as in the MEA system, the H_2S is removed by chemical combining with potassium carbonate and later released by stripping with steam. One significant disadvantage of this method of sweetening natural gas is that an MEA system must follow the potassium carbonate system to remove the final traces of H_2S. Furthermore, a drying system must follow the MEA system to meet pipeline dryness specifications. Finally, CO_2 is also removed from the gas which is a disadvantage with respect to economies of plant installation, operation and gas shrinkage.

The principal object of the invention is to provide an improved process for sweetening and drying natural gas. Further objects are to provide a single treatment system which will remove all contaminating water, H_2S, and mercaptans from th gas stream, and a system which is dry so as to

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minimize corrosion of the equipment. Still another object of the invention is to provide a process for sweetening and drying a natural gas stream, which process in addition to the previously defined characteristics, has a high gas clean-

5   ing efficiency and also permits safe and efficient regeneration of the impurity removal medium. Other objects and advantages of the present invention will be apparent from the subsequent disclosure and appended claims.

In the drawings,

10   Fig. 1 shows water adsorption isotherms for various materials at various temperatures;

Fig. 2 shows hydrogen sulfide isotherms for various materials at various temperatures;

Fig. 3 shows H_2S-CO_2 equilibrium adsorption curves

15   for zeolite 5A;

Fig. 4 shows water adsorption isotherms for various materials at low partial pressures;

Fig. 5 shows hydrogen sulfide isotherms for various materials at low partial pressures; and

20   Fig. 6 is a schematic flowsheet of a process for continuously sweetening and drying natural gas according to the present invention.

It has been unexpectedly found that certain naturally occurring and synthetic zeolites of suitable pore size have a

25   remarkably high affinity for both moisture and the sulfur-containing compounds present in natural gas streams. That is, the pores must be sufficiently large to permit entry of the

water and sulfur compound molecul s. Molecular sieves having

pores with an apparent minimum dimension of at least 5

Angstrom units have been found satisfactory. Furthermore,

they are so constituted in their molecular arrangement of atoms

that they can effect a separation of natural gas, water and

sulfur-containing compounds on the basis of molecular size

and molecular polarity. These particular zeolitic molecular

sieves not only have a high affinity for water and sulfur-

containing compounds but will preferentially adsorb them

rather than other substances of similar molecular dimensions.

In addition, these molecular sieves demonstrate a high water

and sulfur compound capacity at low vapor pressures and at

elevated temperatures, thereby overcoming critical limitations

of prior art natural gas cleanup systems.

The term apparent pore size as used herein may be

defined as the maximum critical dimension of the molecular

species which is adsorbed by the zeolitic molecular sieve in

question under normal conditions. The apparent pore size will

always be larger than the effective pore diameter, which may

be defined as the free diameter of the appropriate silicate

ring in the zeolite structure.

The term "zeolite," in general, refers to a group

of naturally occurring and synthetic hydrated metal alumino-

silicates, many of which are crystalline in structure. There

are, however, significant differences between the various

synthetic and natural materials in chemical composition, crystal

structure and physical properties such as X-ray powder dif-

fraction patterns.

The structure of crystalline zeolitic molecular

sieves may be described as an open thr e-dimensional framework

of SiO_4 and AlO_4 tetrah dra. Th tetrahedra are crosslinked

by the sharing of oxygen atoms, so that th rati of xygen

atoms to the total of the aluminum and silicon atoms is

equal to two, or $O/(Al + Si) = 2$. The negativ lectrovalence

of tetrahedra containing aluminum is balanced by the inclusion within the crystal of cations, for example, alkali metal and alkaline earth metal ions such as sodium, potassium, calcium and magnesium ions. One cation may be exchanged for another by ion-exchange techniques.

The zeolites may be activated by driving off substantially all of the water of hydration. The space remaining in the crystals after activation is available for adsorption of adsorbate molecules. Any of this space not occupied by reduced elemental metal atoms will be available for adsorption of molecules having a size, shape and energy which permits entry of the adsorbate molecules into the pores of the molecular sieves.

The zeolites occur as agglomerates of fine crystals or are synthesized as fine powders and are preferably tableted or pelletized for large scale adsorption uses. Pelletizing methods are known which are very satisfactory because the sorptive character of the zeolite, both with regard to selectivity and capacity, remains essentially unchanged.

The pores size of the zeolitic molecular sieves may be varied by employing different metal cations. For example, sodium zeolite A has an apparent pore size of about 4 Angstrom units whereas calcium zeolite A has an apparent pore size of about 5 Angstrom units, so that only the latter is suitable for practicing the present invention.

Among the naturally occurring zeolitic molecular sieves suitable for use in the present invention are faujasit ,

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erionite and calcium cation-rich chabazite. Th natural
materials are adequately described in th ch mical art. The
preferred synthetic zeolitic molecular sieves include
zeolites L, T, X, Y, and divalent metal cation-exchanged
forms of zeolite A as exemplified by calcium zeolite A.

Zeolite A is a crystalline zeolitic molecular sieve
which may be represented by the formula:

$$1.0 \pm 0.2\frac{M_2O}{n} : Al_2O_3 : 1.85 \pm 0.5 \; SiO_2 \; Y \; H_2O$$
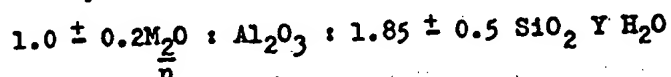
wherein M represents a metal, n is the valence of M, and Y
10 may have any value up to about 6. The as-synthesized zeolite
A contains primarily sodium ions and is designated sodium
zeolite A. Calcium zeolite A is a derivative of sodium
zeolite A in which about 35 per cent or more of the exchange-
able sodium cations have been replaced by calcium. Similarly,
strontium zeolite A and magnesium zeolite A are derivatives
of sodium zeolite A wherein about 35 per cent or more of the
exchangeable sodium ions have been replaced by the strontium
or magnesium ions. Zeolite A is described in more detail in
U.S. Patent No. 2,882,243 issued April 14, 1959.

20 Zeolite T is a synthetic crystalline zeolitic
molecular sieve whose composition may be expressed in terms
of oxide mole ratios, as follows:

$$1.1 \pm 0.4 \; [xNa_2O:(1-x)K_2O]:Al_2O_3:6.9 \pm 0.5 \; SiO_2:yH_2O$$
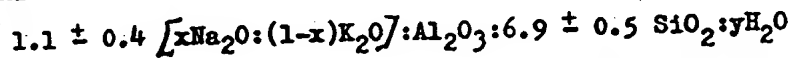
wherein "x" is any value from about 0.1 to about 0.8 and "y"
is any value from about zero to about 8. Further characteriza-
tion of zeolite T by means of X-ray diffraction techniques is

described in U.S. Patent No. 2,950,952.

Zeolite X is a synthetic crystalline zeolitic molecular sieve which may be represented by the formula:

$$0.9 \pm 0.2 \ \frac{M_2O}{n}:Al_2O_3:2.5 \pm 0.5 \ SiO_2:yH_2O$$
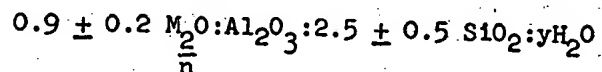
wherein M represents a metal, particularly alkali and alkaline earth metals, n is the valence of M, and y may have any value up to about 8, depending on the identity of M and the degree of hydration of the crystalline zeolite. Sodium zeolite X has an apparent pore size of about 13 Angstrom units. Zeolite X, its X-ray diffraction pattern, its properties, and methods for its preparation are described in detail in U.S.P. No. 2,882,244 issued April 14, 1959.

Zeolite L is described and claimed in Belgian Patent No. 575,117.

Zeolite Y is described and claimed in Belgian Patent Nos. 577,642 and 598,582.

One skilled in the molecular sieve art would normally conclude that sieves having apparent pore sizes of at least 4 Angstrom units would be suitable for adsorbing H_2O and H_2S in accordance with the present invention. This is because the critical dimensions of H_2O and H_2S are approximately 3.1 and 3.6-3.9 Angstrom units, respectively. Furthermore, sodium zeolite A having an apparent pore size of about 4 Angstrom units will adsorb large quantities of H_2S in a static system, wherein the molecular sieve is simply exposed to

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H_2S atmosphere until completely saturated. It will be recognized that static data as measured in a McBain system is commonly employed in the adsorption art to predict the feasibility of dynamic adsorption separations. Contrary to

5 these expectations, it has been found that sodium zeolite A is completely unsuitable for employment in the present invention, because the rate of H_2S adsorption by a 4 Angstrom pore size molecular sieve in a dynamic system is prohibitively low. As used herein, the term "dynamic system" refers to

10 continuous contact between a moving gas feed stream and a zeolitic molecular sieve bed. Also, the term "critical dimension" refers to the diameter of the circumscribed circle of the cross section of the adsorbate molecule's minimum area. These are calculated from available bond lengths, bond

15 angles and van der Waals radii.

Furthermore, it has been discovered that when mercaptans are present in the feed gas in excessive quantities, they are most efficiently removed by zeolitic molecular sieves having an apparent pore size of at least 9 Angstrom units,

20 as for example synthetic crystalline zeolites X, Y and L. This is probably due to a combination of the previously discussed adsorption rate effect, and the fact that mercaptans have larger critical dimensions than H_2S.

This invention contemplates a method for simultane-

25 ously removing moisture and sulfur-containing compounds from a natural gas stream comprising the steps of providing a bed of crystalline zeolitic molecular sieve material having an

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apparent pore size of at least 5 Angstrom units. A moisture
and sulfur compound containing natural gas streams is
provided and contacted with the zeolitic molecular sieve bed,
and a gas stream depleted of such impurities is discharged
from the bed. Certain critical operating conditions to pro-
vide maximum efficiency have also been discovered; these
criticalities will be discussed later in detail.

The invention also provides a method for continu-
ously removing moisture and sulfur-containing compounds from
10   a natural gas stream in which at least two separate zones are
provided, each containing a bed of crystalline zeolitic
molecular sieve material having an apparent pore size of at
least 5 Angstrom units. The feed gas stream is contacted
with a first zeolitic molecular sieve bed as an adsorption
stroke, thereby adsorbing at least most of the moisture and
sulfur-containing compounds. An impurity-depleted natural
gas product stream is discharged from the first bed. As a
desorption stroke, a heated fluid is simultaneously passed in
indirect heat exchange with a second zeolitic molecular sieve
20   bed having previously been loaded with moisture and sulfur-
containing compounds. A heated desorbing purge gas is passed
in direct contact with the second bed thereby removing the
deposited materials. The desorption stroke is continued until
the desorbed second bed reaches a temperature of at least
300°F., at which point the bed is recooled by passing a portion
of the moisture and sulfur compound-depleted natural gas
product stream therethrough. The flows between the first and

redooled second beds ar periodically switched thereby pass-
ing the gas feed stream to the second bed as an adsorption
stroke and passing the heated fluid and heated desorbing
purge gases in contact with the first bed as a desorption
stroke.

As used in the specification and ensuing claims, the
expression "natural gas stream" refers to a mixture of gases
comprising primarily methane with traces of at least the
following components as minor constituents: nitrogen, carbon
10 monoxide, carbon dioxide and ethane.

The previously discussed criticality of molecular
sieve pore sizes was clearly illustrated in a series of tests
involving synthetic zeolites 4A, 5A and 13X, the numerals in
the designations indicating the approximate pore size and
the letters identifying the type of zeolite, as previously
defined. The H_2S breakthrough capacity of these zeolites
was determined on a natural gas stream at the following
operating conditions:

TABLE I

20 Adsorbent	- 1/16 in. pellets activated at 450°F. with a clean dry natural gas stream.
Column	- 6 ft. long x 1.5 in. inside diameter.
Stream Analysis	- Methane - 99.62 mol-% Ethane - 0.08 mol-% Propane and Higher - 0.005 mol-% CO_2 - 0.2 mol-% H_2S - 0.11 mol-%
Flow Rate	- 2055 lb/hr/ft.^{2}
Pressure	- 460-500 psig.
Temperature	- 60-70°F.

The following r sults were obtained:

Type of Sieve	4A	5A	13X
% Loading of Breakthrough (lb/100 lb. of molecular sieve)	2.43	6.25	6.50
Effluent H_2S Concentration Before Breakthrough (ppm.)	0.3-4	0.3-4	0.3-4
Effluent H_2O Concentration Before Breakthrough (ppm.)	1 ppm	1 ppm	1 ppm

These data indicate that at the indicated test conditions, zeolites 5A and 13X exhibit remarkably higher dynamic capacity than zeolite 4A, since the former will ad- sorb at least 2-1/2 times as much H_2S as zeolite 4A.

Molecular sieve zeolite 5A has successfully re- moved H_2S and water from gas streams at temperatures as low as 60°F. and as high as 175°F., but these by no means represent functional limits. However, at an adsorption temperature of 175°F. the separation takes place at a con- siderable sacrifice in capacity. This is apparent from two tests made at identical conditions except for adsorption temperature. At a temperature of 80°F., the H_2S capacity at breakthrough was 8.6 lbs/100 lbs. of adsorbent, and at 175°F. the H_2S capacity was 5.4 lbs.

Fig. 1 shows water adsorption isotherms for zeolite 5A, silica gel, and activated alumina at temperatures of 77°F., 167°F. and 302°F. with lbs. of water adsorbed per 100 lbs. of dry adsorbent being plotted against the water vapor pressure in mm. of Hg. Inspection of these curves indicates that, for example at 167°F. and a vapor pressure of

20 mm. Hg., the respective capaciti s of zeolite 5A, silica gel, and activated alumina are 17, 4 and 3 lbs. H_2O per 100 lbs. of dry adsorbent.

Fig. 2 shows hydrogen sulfide isotherms for zeolite 5A, silica gel and activated alumina at temperatures of $77°F.$, $167°F.$ and $302 °F.$ with lbs. of H_2S adsorbed per 100 lbs. of dry adsorbent being plotted against the H_2S vapor pressure in mm. of Hg. Inspection of these curves indicates that, for example at $167°F.$ and a vapor pressure of 150 mm. Hg., the

10   respective capacities of zeolite 5A and silica gel are 12.2 and 0.8 lbs. H2S per 100 lbs. of dry adsorbent.

With regard to operating pressures, it has been found that the water and sulfur compound separation efficiency and capacity of the present zeolitic molecular sieves is not appreciably affected by the total pressure of the natural gas streams, if the other variables such as component partial pressures, temperature, linear velocity and the like, are held constant.

The capacity of the present zeolitic molecular

20   sieves for H_2S is affected by the amount of carbon dioxide (CO_2) in the natural gas stream. This will be apparent from an inspection of Fig. 3 which presents H_2S - CO_2 equilibrium adsorption curves for zeolite 5A at $70°F.$ and 1 atmosphere pressure. The curve shows that although H_2S is preferentially adsorbed, simultaneous adsorption occurs. In natural gas streams containing 0.08 mol-% H_2S and 0.92 mol-% CO_2 the mole fraction of the H_2S on the adsorbent is 0.5, the remainder

being CO_2. However, in a natural gas stream containing 0.8% H_2S and 0.2% CO_2 the mole fraction of H_2S on the zeolitic molecular sieve adsorbent would be 0.97. The effect of CO_2 on the capacity of zeolite 5A for H_2S in a dynamic system is shown in the following Table II:

TABLE II

Test Conditions:

Adsorbent	– Zeolite 5A – 1/16" pellets activated at 600°F.	
Column	– 24 in. long by 1.049 in. I.D.	
Pressure	– Atmospheric	
Adsorption Temperature	– 72°F	
Superficial Linear Velocity	– 0.32 ft./sec.	

Results:

Stream Analysis	94.3% N_2 5.7% H_2S	89 % N_2 5.7% H_2S 5.3% CO_2
% H_2S Loading at Breakthrough	9.65	7.2

Based on Fig. 3, the preferred composition range of H_2S–CO_2 mixtures is between 0.1 and 1.0 mole fraction of H_2S in the vapor, although separation could be effected below 0.1 mole fraction of H_2S in the vapor. However, the capacity reduction by virtue of the simultaneous adsorption of CO_2 in such low H_2S concentrations would probably be prohibitive as the ratio of H_2S to H_2S + CO_2 in the vapor is reduced below 0.1. The H_2S loading in this range begins to desorb off rapidly in favor of the CO_2 loading.

As previously discussed, certain zeolitic molecular
sieves have a high affinity for water and hydrogen sulfide,
and will preferentially adsorb them rather than the other
natural gas constituents, even though some of the latter
have molecular dimensions similar to water and hydrogen sul-
fide, as for example nitrogen and methane. In addition,
these same zeolitic molecular sieves demonstrate high capaci-
ties for the above-mentioned impurities at low partial pressures.
This remarkable and unexpected characteristic is clearly
illustrated in Figs. 4 and 5, which represent tests on
zeolite 5A and 13X, and comparisons with the behavior of
alumina and silica gel under the same conditions. Similar
behavior is shown by the other crystalline zeolitic molecular
sieves having apparent pore sizes of at least 5 Angstrom units.

Fig. 4 shows water adsorption isotherms for zeolite
5A, zeolite 13X, silica gel and activated alumina at a temper-
ature of 77°F. (25°C.) over a water partial pressure range of
0 to 3.0 mm. Hg. An inspection of Fig. 4 will reveal the
remarkably high capacities of zeolites 5A and 13X for water
at low vapor pressures as compared to conventional adsorbents.
For example, at a water vapor pressure of 0.2 mm. Hg., the
capacities of zeolites 5A and 13X are about 17.7 lbs. and
18.6 lbs. respectively, whereas the capacities of activated
alumina and silica gel are about 3.5 lbs. and 2.8 lbs. of water
respectively. This means that the water capacity of the
present zeolitic molecular sieves is at least 4 times that
of commonly employed adsorbents at 0.2 mm. Hg. There ar

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frequent industrial situations wherein an inlet natural gas
has a relatively small moisture content below about 50 mm.
Hg. at 77°F., but where even such water traces are detrimental
to the apparatus in which the gas is to be processed. One

5   situation of this type is a low temperature natural gas dis-
tillation column, where very small quantities of water could
freeze out on the liquid-gas contact surfaces and eventually
cause shutdown. The present invention obviates this problem
by providing an adsorption process which substantially com-

10 pletely removes hydrogen sulfide and water traces to below
4 ppm. and 1 ppm., respectively, in a highly efficient
manner.

Fig. 5 shows hydrogen sulfide isotherms for zeolite
5A, zeolite 13X, silica gel and activated alumina at a temper-

15 ature of 77°F. (25°C.) over a hydrogen sulfide partial
pressure range of 0 to 3.0 mm. Hg. It is apparent that at
77°F., both zeolite 5A and zeolite 13X have an appreciable
capacity for H_2S at as low as 0.5 mm. partial pressure, al-
though separations of H_2S from natural gas could be effected

20 at partial pressures lower than 0.5 mm. The preferred range
of H_2S concentrations (mol-%) in natural gas streams depends
upon the total pressure of the system. For example, the
partial pressure of H_2S and capacity containing 0.01 mol-%
H_2S at atmospheric pressure would be 0.076 mm. and 0.5 lbs.

25 per 100 lbs. of molecular sieve. At 20 atmospheres operating
pressure the partial pressure of H_2S would be 1.52 mm. and
capacity would be 5.1 lbs. H_2S per 100 lbs. of molecular sieve.

Another important feature of the present invention
is a method of desorbing the H_2S, mercaptans and water from
the impurity-loaded zeolitic molecular sieve bed. The
prior art has employed vacuum pressures for this purpose,
5   but such a procedure is somewhat undesirable because of the
possibility of leaks in the system creating a potential ex-
plosive mixture of methane (the major constituent of natural
gas) and air. Also, desorption by heat alone is undesirable
because if H_2S remains in the bed as the adsorbent is cooled,
10   the H_2S is adsorbed reducing the capacity of the adsorbent.
To eliminate these problems, the present method contemplates
desorption of the impurity loaded zeolitic molecular sieve bed
by simultaneously passing a heated fluid in indirect heat
exchange with the bed, and passing a heated desorbing purge
15   gas in direct contact with such bed. By "indirect heat ex-
change" is meant passage through pipes or coils embedded in
the zeolitic molecular sieve bed, so that the heated fluid
transfers heat through the conduit walls into the sieve bed,
but never physically contacts such bed. In contrast, a hot
20   desorbing purge gas simultaneously flows through the bed it-
self in intimate direct contact with the sieve material and
thereby sweeps out the desorbed moisture and sulfur-containing
gas. The purge gas flow may be relatively small; that is,
just enough to facilitate efficient heat transfer and remove
25   the impurities. For example, when the moisture and sulfur
compound-depleted product stream is employed as the purge
gas, no more than about 3% of the product is required for the

~149°C

purging function. The desorption step is continued until
the bed reaches a temperature of at least 300°F., at which
point the desorbed bed is recooled by passing at least a
portion of the moisture and sulfur compound-depleted natural
5   gas product stream through the bed. When recooling is
complete, the bed may be placed back on the adsorption stroke.

Features of the invention are illustrated by the
following specific examples:

        Example I - Removal of Hydrogen Sulfide and Water
                 from Natural Gas with 5A, 1/16 inch
10   Zeolitic Molecular Sieve:

A stainless steel column 1.5 inches inside diameter
by 6 feet long was filled with 1,451 grams of activated 5A,
1/16 inch zeolitic molecular sieve. At a pressure of 495
psig. "sour" natural gas containing 0.1% H_2S and 718 ppm.
15   water was passed through the bed at a flow rate of 595 cfh.
The effluent concentration of H_2S was measured as a function
of time and was reduced from 0.1% (1000 ppm.) to 0.4-4.0 ppm.
by volume for 2.65 hours, at which point the effluent concen-
tration increased until after 4.83 hours the effluent concen-
20   tration of H_2S was equal to the inlet concentration. During
the entire test the effluent water concentration remained
below 1.0 ppm. by volume compared with an inlet concentration
of 718 ppm. In this and the succeeding examples, "break-
through" is the point at which the effluent H_2S concentration
25   exceeds 4 ppm. A tabular summary of the test run follows:

Gas Temperature	65°F. 18°C
Mass Velocity (lb/hr/ft.^{2})	2055
Superficial Linear Velocity (ft/sec.)	0.39
Breakthrough Capacity (lb. H_2S/100 lb. of Dry Bed)	6.25
Effluent H_2S Concentration before Breakthrough (ppm)	0.4-4.0

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Example II - Removal of Hydrogen Sulfide and Water
from Natural Gas with 13X, 1/16 inch
Zeolitic Molecular Sieve:

A 1.5 inch I.D. x 6 feet long stainless steel
column was filled with 1,336 grams of activated 13X, 1/16 inch
molecular sieve pellets. A pressure of 490 psig. "sour"
natural gas containing 0.0996% (996 ppm. by volume) H_2S and
718 ppm. water was passed through the bed at a flow rate of
595 cfh. The effluent concentration of H_2S was measured as
a function of time and was reduced from 996 ppm. to between
0.4-4 ppm. by volume for a period of 3.68 hours before break-
through occurred. The data are summarized as follows:

Gas Temperature   66-67°F.
Mass Velocity($lb/hr/ft.^2$)   2055
Superficial Linear Velocity (ft/sec.)   0.39
Breakthrough capacity (lb. H_2S/100 lb. of   6.50%
  Dry Bed)
Effluent H_2S before Breakthrough (ppm)   0.15-4.0
Effluent H_2O before Breakthrough (ppm)   <1 ppm.

Example III - Removal of Hydrogen Sulfide and Water
from Natural Gas with 5A, 1/16 inch
Zeolitic Molecular Sieve Using a 2-1/2
Foot I.D. by 7.25 Foot Long Column:

A steel column 2-1/2 ft. in diameter by 7.25 feet
long was filled with 870 pounds of 5A, 1/16 inch molecular
sieve pellets. The bed was activated at 450°F. by passing
clean dry natural gas through the bed. At a pressure of 440
psig. "sour" natural gas containing 0.1% H_2S and 1790 ppm.
H_2O was passed through the bed at a flow rate of 108,333 scfh.
The effluent H_2S concentration was measured as a function of
time and was reduced from 0.1% to 0.4-4 ppm. by volume for a
period of 2.23 hours before breakthrough occurred. The

effluent water concentration remained 1 ppm. for the entire run. The breakthrough loading on this test was 3.52 pounds of H$_2$S/100 lb. dry adsorbent.

The present invention also provides a process for

5   continuously sweetening and drying a natural gas stream by advantageously and efficiently employing zeolitic molecular sieve adsorbents having an apparent pore size of at least 5 Angstrom units. Referring now more specifically to Fig. 6, the inlet natural gas is introduced through conduit 10. . If

10   the inlet gas is not already in a state of substantial compression, such gas is directed through compressor 11 for compression preferably to a level of about 100 to 1,000 psig. The compressed gas may be directed through an aftercooler if desired (not shown). The compressed inlet gas is directed

15   through three-way control valve 12 to a first zeolitic molecular sieve bed 13. Moisture and sulfur-containing compounds as for example hydrogen sulfide and mercaptans are selectively adsorbed by the zeolitic molecular sieve material having apparent pore sizes of at least 5 Angstrom units. The

20   resulting moisture and sulfur compound depleted natural gas product is discharged from the bed through branch conduit 14, switching valve 15 and communicating discharge conduit 16, and contains less than one ppm. by volume of such impurities.

While first bed 13 is on the adsorption stroke as

25   previously described, second zeolitic molecular sieve bed 17 is on a reactivation or desorption stroke. This is accomplished by the introduction of a heated fluid through conduit 18 and

control valve 18a to coils 19 embedded in the second bed 17.
The heated fluid may for example be hot oil at a temperature
of 300 to 600°F., and such oil preferably flows in a direc-
tion countercurrent to the inlet natural gas. The heated
fluid in embedded coils 19 indirectly exchanges heat with
the impurity loaded second zeolitic molecular sieve bed 17,
and is withdrawn through conduit 20 for processing as desired.
It is to be noted that the circulating fluid is not con-
taminated with the natural gas impurities, and consequently
may be reheated and recirculated to inlet conduit 18 if de-
sired.

Simultaneously with the circulation of the in-
directly heat exchanging fluid in coils 19, a heated desorb-
ing purge gas is introduced to the system through conduit
21, three-way control valve 22 therein, and communicating
branch conduit 23 to the impurity-laden second zeolitic
molecular sieve bed 17 for removal of the moisture and sulfur-
containing compounds therefrom. The purge gas preferably
flows countercurrent to the direction of inlet natural gas,
and parallel to the flow direction of the heated fluid in
coils 19. The impurity-laden purge gas is discharged from
second bed 17 into conduit 24 and through control valve 25
to discharge conduit 26 for use as desired. The preferred
purge gas is a small portion of the impurity-free product
natural gas having previously been discharged from the first
bed 13 through conduit 16. It is of course desirable to
use as small a fraction of the product gas as possible for
the purging and less than about 3% of the product gas is needed

for this function. To this end, a small portion of th
product gas stream may be diverted from discharge conduit 16
through branch conduit 16a and control valve 16b for passage
to a heater (not shown). The resulting heated clean gas may
then be returned through conduit 21. The circulating purge
gas also serves to increase the heat transfer rate from
heated fluid in coils 19 to the desorbing molecular sieve
bed 17.

As previously discussed, the desorption step should

10   be conducted at a temperature of at least $300^\circ F.$, and
preferably in the range of 300 to $600^\circ F.$ to insure substan-
tially complete removal of the moisture and sulfur compound
impurities from the second bed. If the desorption temperature
is below $300^\circ F.$, the impurities are purged at a prohibitively
low rate, whereas a desorption temperature above $600^\circ F.$
produces hydrolytic damage to the zeolitic cell structure and
consequent loss of adsorptive capacity. After desorption the
adsorbent bed 17 is recooled to its adsorption or operating
temperature by terminating the heating fluid and purge gas

20   flows by closing valves 18a and 22, respectively. Relatively
cool product gas is then diverted from discharge conduit 14
through branch conduit 27 and control valve 28 to communicating
conduit 29 having switching valve 30 therein. The product
gas then flows through heated, reactivated second bed 17 and
thereby recools such bed to the adsorption operating tempera-
ture. The cooldown product gas preferably flows in the same
direction as the inlet feed gas, and is discharged from bed

17 into conduit 31 for passage to communicating discharge conduit 16.

After a period of time, depending upon the inlet concentration of the contaminants, the adsorption pressure, the amount of adsorbent, and the flow rate of the inlet gas, the quantity of moisture and sulfur-containing compounds in the product gas increases. When these concentrations reach the permissible limit, the flows are switched so that the first bed 13 is placed on desorption stroke, and second bed 17 is placed on adsorption stroke. This is accomplished by closing switching valve 15 at the discharge end of first bed 13 and opening corresponding switching valve 32 at the discharge end of second bed 17. Also, the position of three-way valve 12 at the inlet end is changed so as to permit flow of the inlet natural gas therethrough to conduit 33, communicating at the opposite end with second bed 17.

The first zeolitic molecular sieve bed 13 is purged and recooled in a manner analogous to that of second bed 17 as previously described. More specifically, the heating fluid is introduced through conduit 18, communicating branch conduit 34, control valve 35 therein, and coils 36 embedded in second bed 13. Also, the hot purge gas is introduced through conduit 21, three-way valve 22 and communicating conduit 37 to first bed 13 for flow therethrough. The resulting impurity-laden purge is discharged from first bed 13 into conduit 38 communicating with three-way valve 25, which is connected to discharg conduit 26. During cooldown, a

24.

1   small portion of the product gas is directed through conduit
27 and branch conduit 29 to switching valve 39 for flow
through first bed 13.

In summary, the present invention affords a single-
step adsorbent system for removing contaminated water and
sulfur-containing compounds from a natural gas stream. The
adsorbent, zeolitic molecular sieves having apparent pore
sizes of at least 5 Angstrom units, has a remarkably high
capacity for these impurities, even after many reactivations.

10 A method of desorbing an impurity-laden zeolitic molecular
sieve bed is provided which is highly efficient and effec-
tive. Finally, the present dry system of purification mini-
mizes corrosion of the processing equipment, which is a
serious disadvantage of prior art liquid systems for purify-
ing natural gas streams.

Although the preferred embodiments have been
described in detail, it is contemplated that modifications
of the process may be made and that some features may be
employed without others, all within the spirit and scope

20 of the invention as set forth herein.

THE EMBODIMENTS OF THIS INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method for simultaneously removing moisture
and sulfur-containing compounds from a natural gas stream
comprising the steps of providing a bed of crystalline
zeolitic molecular sieve material having an apparent pore
size of at least 5 Angstrom units; providing a moisture
and sulfur compound-containing natural gas feed stream and
contacting such stream with the zeolitic molecular sieve
bed as an adsorption stroke; discharging a moisture and
sulfur compound-depleted natural gas stream from such bed;
continuing such feed stream contact and discharge until the
moisture and sulfur compound concentration in the discharge
gas reaches a predetermined value; as a desorption stroke,
simultaneouly passing a heated fluid in indirect heat
exchange with the moisture and sulfur-compound loaded bed,
and passing a heated desorbing purge gas in direct contact
with such bed thereby removing the adsorbed moisture and
sulfur-containing compounds; continuing said desorption
stroke until the desorbed bed reaches a temperature of at
least 300°F.; recooling said desorbed bed by passing at
least a portion of said moisture and sulfur compound-
depleted natural gas stream therethrough; discharging such
recooling portion from said desorbed bed; and thereafter
returning the r cooled crystalline zeolitic molecular
siev bed to said adsorption stroke.

2. A method according to claim 1 in which the zeolite is a member selected from the group consisting of crystalline calcium zeolite A having an apparent pore size of about 5 Angstrom units, and crystalline sodium zeolite X having an apparent pore size of at least 9 Angstrom units.

3. A method according to claim 1 in which the zeolitic molecular sieve bed is heated to a temperature of 300 to 600°F. during the desorption stroke.

4. A method according to claim 1 in which the purge gas is a portion of said moisture and sulfur compound-depleted natural gas stream comprising less than about 3% by volume of such stream, and said portion is heated prior to purging said zeolitic molecular sieve bed.

5. A method for continuously removing moisture and sulfur-containing compounds from a natural gas stream comprising the steps of providing at least two separate zones each containing a bed of crystalline zeolitic molecular sieve material having an apparent pore size of at least 5 Angstrom units; providing a moisture and sulfur compound-containing natural gas feed stream and contacting such stream with a first zeolitic molecular sieve bed as an adsorption stroke, thereby adsorbing at least most of said moisture and sulfur-c ntaining compounds; discharging a moisture and sulfur compound-d pl ted natural gas product stream from the first bed having a moisture c ntent f less

than about 1 ppm. and an equivalent H_2S content of less than about 4 ppm.; as a desorption stroke, simultaneously passing a heated fluid in indirect heat exchange with a second zeolitic molecular sieve bed having previously been loaded with moisture and sulfur-containing compounds, and passing a heated desorbing purge gas in direct contact with the second bed thereby removing the adsorbed moisture and sulfur-containing compounds; continuing said desorption stroke until the desorbed second bed reaches a temperature of at least 300°F.; recooling said desorbed second bed by passing at least a portion of said moisture and sulfur compound-depleted natural gas product stream therethrough; discharging such recooling portion from said desorbed second bed; and periodically switching the flows between the first and recooled second beds thereby passing the gas feed stream to said second bed as an adsorption stroke and passing said heated fluid and heated desorbing purge gases in contact with said first bed as a desorption stroke.

6. A method according to claim 5 in which the zeolite is a member selected from the group consisting of crystalline calcium zeolite A having an apparent pore size of about 5 Angstrom units, and crystalline zeolite X having an apparent pore size of at least 9 Angstrom units; the purge gas is a portion of said moistur and sulfur compound-depleted natural gas pr duct stream comprising less than

1　about 3% by volume of such stream; and the zeolitic molecular sieve beds are heated to a temperature of 300 to 600°F. during the desorption stroke.

　　　7.　A method according to claim 6 in which the zeolite is crystalline calcium zeolite A having an apparent pore size of about 5 Angstrom units.

　　　8.　A method according to claim 6 in which the
10　zeolite is crystalline zeolite X having an apparent pore size of at least 9 Angstrom units.

20

30

FIG.I.
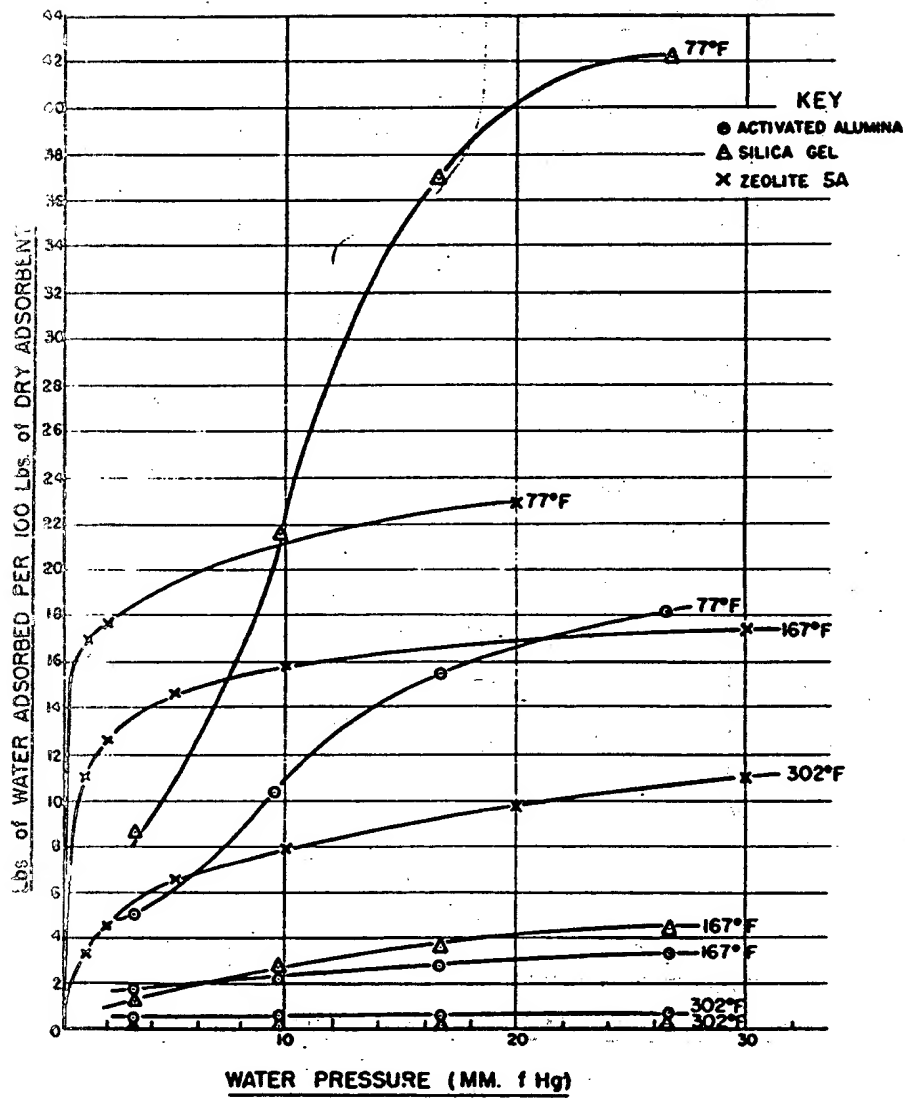
WATER ADSORPTION ISOTHERMS
For Various Materials

KEY
⊙ ACTIVATED ALUMINA
△ SILICA GEL
✕ ZEOLITE 5A

Lbs. of WATER ADSORBED PER 100 Lbs. of DRY ADSORBENT

WATER PRESSURE (MM. f Hg)

FIG.2.

HYDROGEN SULFIDE ADSORPTION ISOTHERMS
For Various Materials

KEY
⊖ ACTIVATED CARBON
△ SILICA GEL
✕ ZEOLITE 5A

Lbs. of HYDROGEN SULFIDE ADSORBED PER 100 Lbs. of DRY ADSORBENT

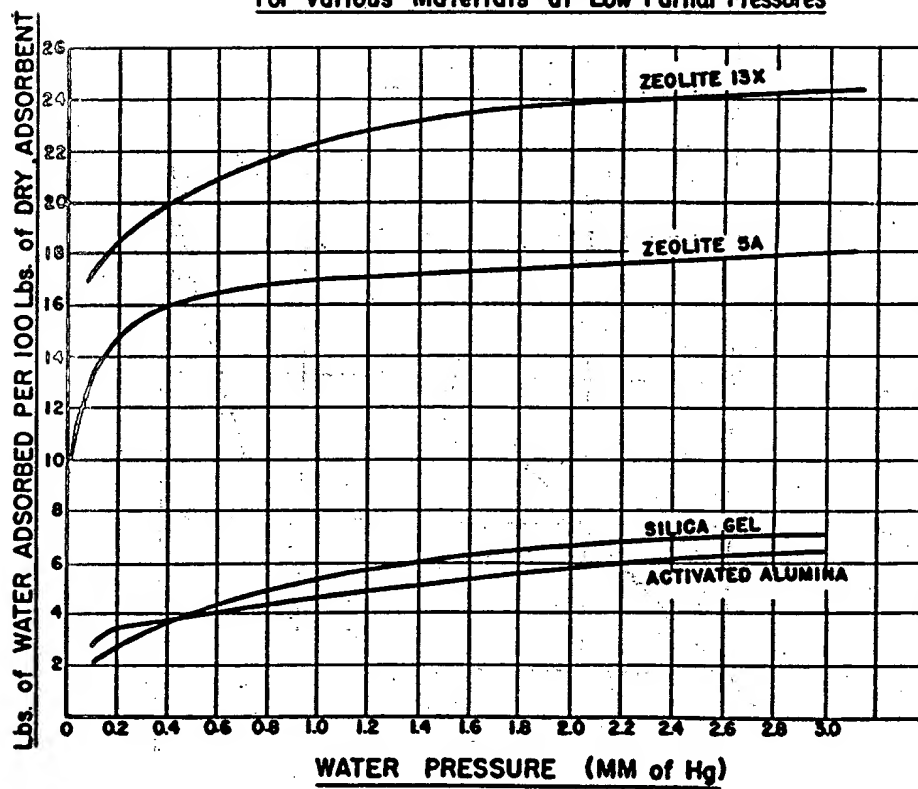HYDROGEN SULFIDE PRESSURE (MM of Hg)
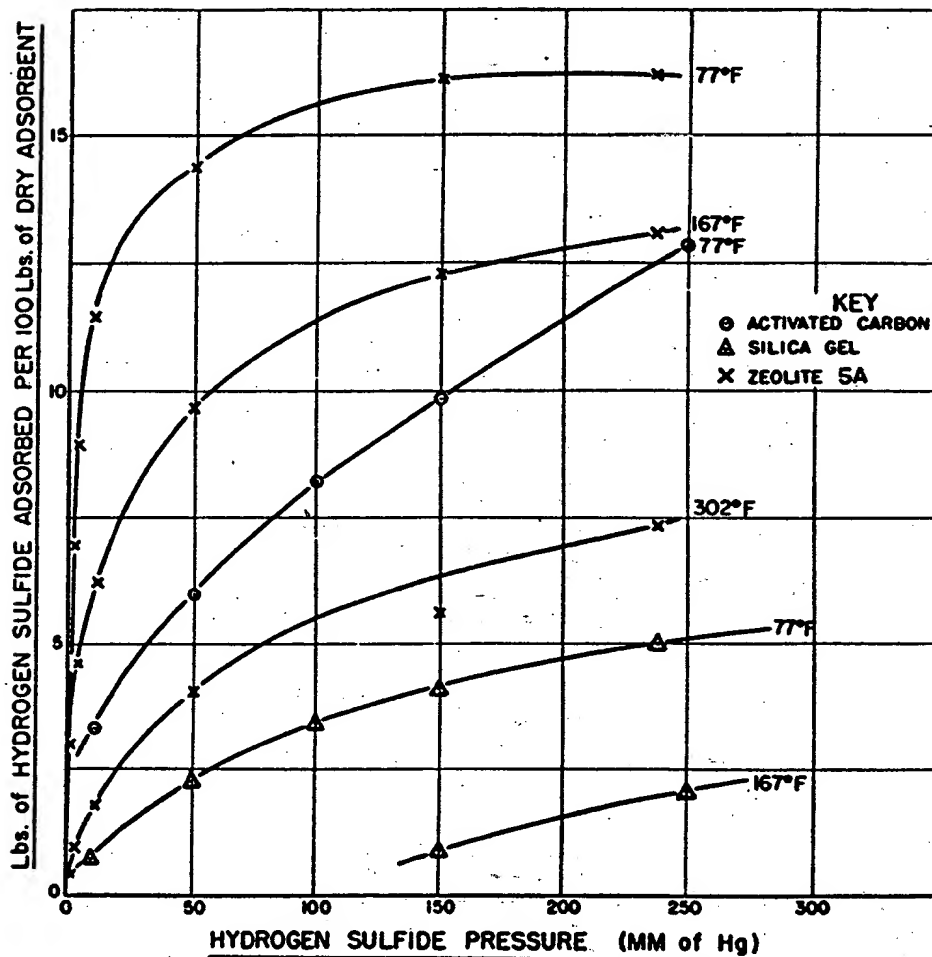
FIG.3.

HYDROGEN SULFIDE – CARBON DIOXIDE
EQUALIBRIUM ADSORPTION – 70°F., I ATM
For Zeolite 5A
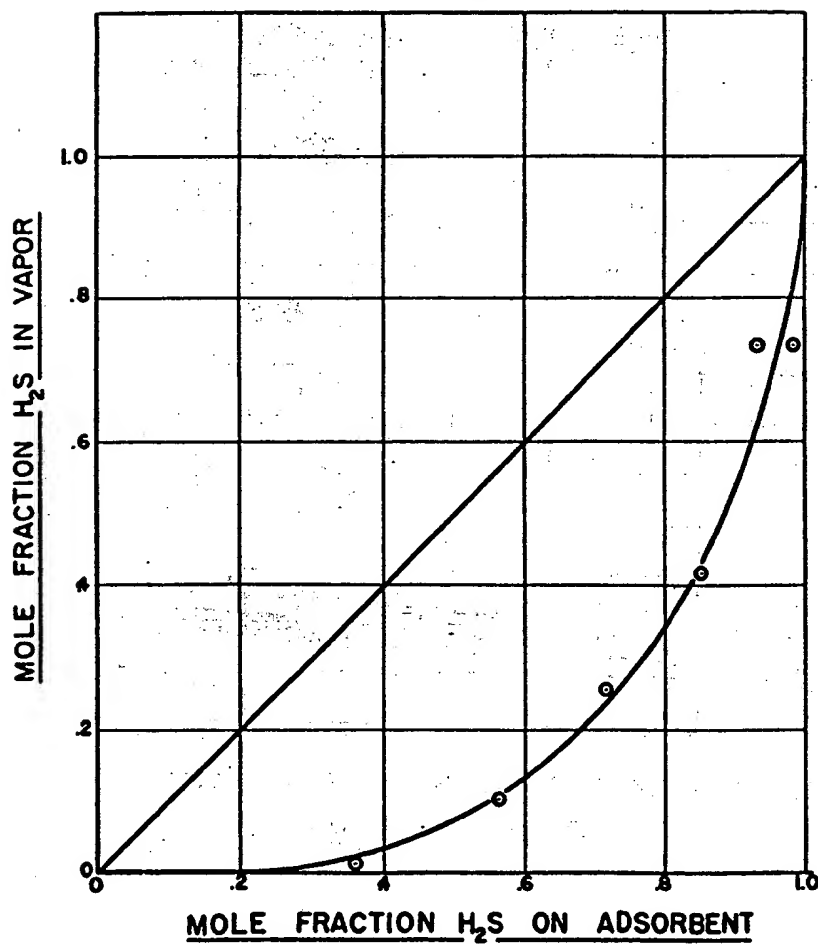
FIG. 4.

WATER ADSORPTION ISOTHERMS
For Various Materials at Low Partial Pressures

FIG.5.

HYDROGEN SULFIDE ADSORPTION ISOTHERMS
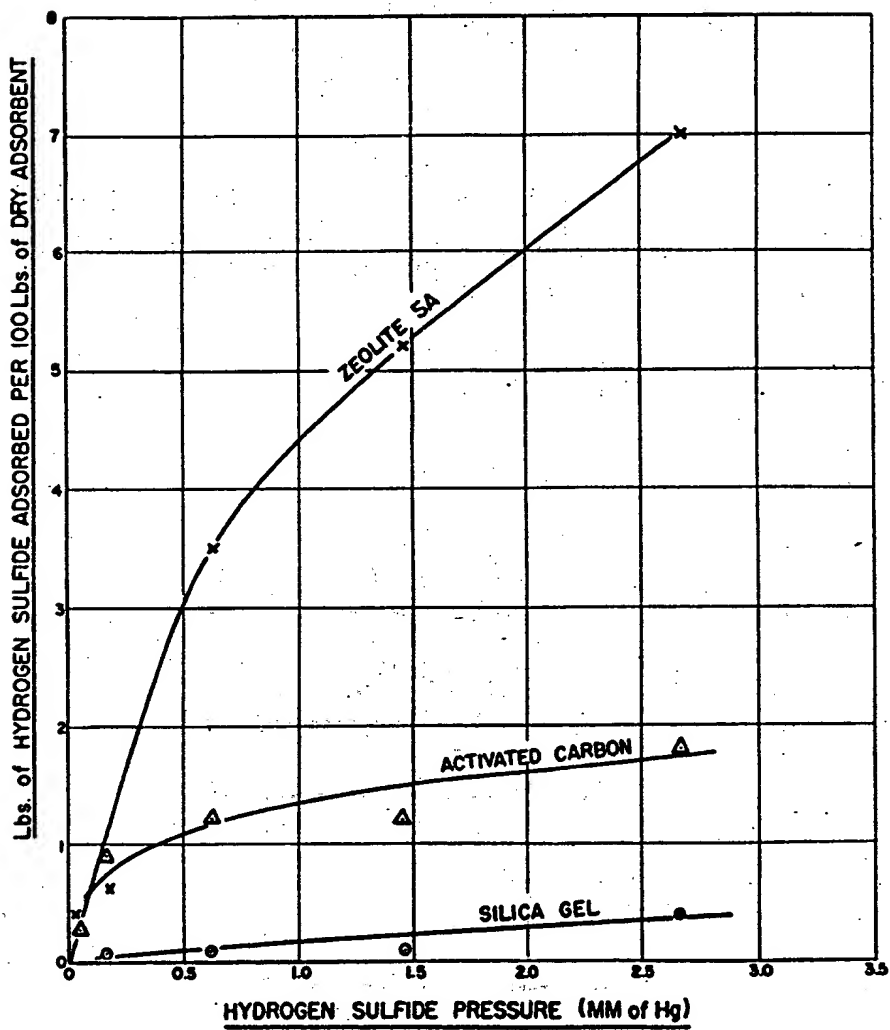### For Various Materials at Low Partial Pressures

HYDROGEN SULFIDE PRESSURE (MM of Hg)

FIG.6.